

Structure of Tetrakis(methylamino)silane

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Abstract. $C_4H_{16}N_4Si$, $M_r = 148.3$, tetragonal, $I4_1/a$, $a = 9.301(55)$, $c = 10.075(61)$ Å, $V = 870.48(81)$ Å³, $Z = 4$, $D_x = 1.1315$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.68$ cm⁻¹, $F(000) = 328$, room temperature, final $R = 0.0427$, $wR = 0.0478$ for 521 observed reflections and 29 variables, $F(hkl) > 4\sigma(F)$. Si is coordinated by four N atoms at a bonding distance of 1.701(1) Å. The Si atom resides on a crystallographic fourfold inversion axis. Amino-group H atoms lie 0.442 Å above Si—N—C planes. The calculated orientation of the methyl groups is confirmed by difference Fourier analysis.

Experimental. $Si(NHCH_3)_4$ was isolated as the major product from the reaction of $SiCl_4$ with CH_3NH_2 in *n*-pentane. Transparent colourless crystals were obtained by sublimation. Crystal $0.4 \times 0.4 \times 0.5$ mm. Automated Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters determined using 25 reflections in the range $6 < \theta < 15^\circ$. Data corrected for Lorentz and polarization effects, absorption ignored. $2\theta_{\text{max}} = 56^\circ$, range of hkl : $0 \leq h \leq 10$, $-12 \leq k \leq 12$, $-13 \leq l \leq$

13. Two standard reflections measured every 75 reflections showed no significant loss in intensity over data collection. $\omega/2\theta$ scan technique. Total of 2218 reflections measured, 521 unique (non-zero), 446 observed with $F(hkl) > 4\sigma(F)$. Structure solved by direct methods, full-matrix least-squares refinement on F of 29 parameters (SHELX76, Sheldrick, 1976), $w^{-1} = [\sigma^2(F) + 0.01034|F_o|^2]$ on a VAX11/750 computer. Coordinates and anisotropic displacement parameters refined for non-H atoms; position of amino-group H atom, H(1), from difference Fourier map and refined with isotropic U ; H atoms of methyl groups in calculated positions with fixed isotropic $U = 0.17$ Å². $R = 0.0427$, $wR = 0.0478$, $R_{\text{int}} = 0.070$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $\Delta\rho_{\text{max}} = 0.18$,

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Table 1. Fractional coordinates and equivalent isotropic displacement coefficients for non-H atoms

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Si(1)	0.0000	0.2500	0.6250	0.0365 (3)
N(1)	0.1353 (1)	0.3349 (1)	0.5423 (1)	0.0523 (5)
C(1)	0.2454 (2)	0.2631 (2)	0.4646 (2)	0.0656 (7)
H(1)	0.1246 (27)	0.4274 (31)	0.5142 (26)	0.0662 (69)

Table 2. Bond lengths (Å) and angles (°)

Si(1)—N(1)	1.701 (1)	H(1)—N(1)	0.911 (30)
N(1)—C(1)	1.451 (2)		
Si(1)—N(1)—C(1)	124.9 (1)	N(1)—Si(1)—N(1'')	103.8 (1)
N(1)—Si(1)—N(1')	121.4 (1)	H(1)—N(1)—Si(1)	120.5 (1.6)
N(1)—Si(1)—N(1''')	103.9 (1)	C(1)—H(1)—H(1)	110.1 (1.6)

Symmetry code: (') $-x, \frac{1}{2}-y, z$; (')' $\frac{3}{4}+y, \frac{3}{4}-x, \frac{3}{4}-z$; (')'' $\frac{1}{4}-y, \frac{1}{4}+x, \frac{3}{4}-z$.

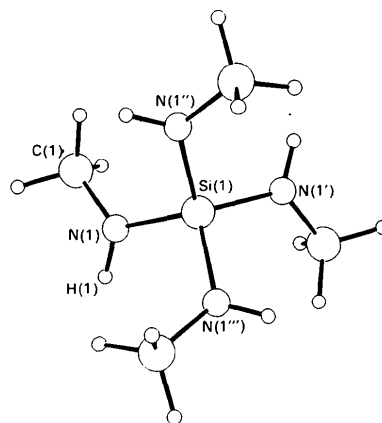


Fig. 1. Perspective view of the title compound.

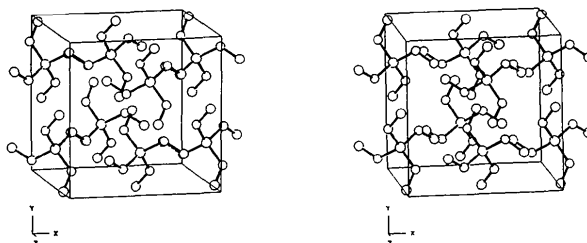


Fig. 2. Stereoscopic view of crystal packing.

$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$; atomic scattering factors were those incorporated in *SHELX76*.

Final atomic positional and isotropic displacement parameters for non-H atoms are given in Table 1. Table 2 lists interatomic distances and valence angles. Drawings of $\text{Si}(\text{NHCH}_3)_4$ are shown in Figs. 1 and 2.*

Related literature. The reactions of SiCl_4 with CH_3NH_2 in the gas phase (Drake & Westwood, 1971), without solvent at room temperature (Hagen & Callaway, 1972), in *n*-pentane (Andersch & Jansen, 1990) and in petroleum ether (Adrianov, Il'in, Talanov, Isakova & Sidorenko, 1976) have been reported in the literature. Based on an elementary analysis Adrianov suggested the same composition as determined for the title compound

* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53013 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for one of his products; however, no information about the molecular structure was given.

The electronic structures of SiR_4 ($R = \text{Me, Ph, NH-Ph, OPh}$) have been discussed by Tatevosyan, Shuvalev & Kopylov (1982). One mole of SiCl_4 combines with four moles of $R(\text{C}_6\text{H}_4)\text{NH}_2$ ($R = o\text{-Et, NO}_2, p\text{-CHO}$) when mixed in benzene to give coloured, fairly stable, complexes (Pandey, 1972).

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Structural refinement of Y_2BaCuO_5 using neutron powder diffraction. By SHIYOU PEI,* A. P. PAULIKAS,† B. W. VEAL† and J. D. JORGENSEN,† *Science and Technology Center for Superconductivity and Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA*

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Abstract

$M_r = 458.49$, orthorhombic, *Pbnm*, $a = 7.1342$ (1), $b = 12.1811$ (1), $c = 5.6580$ (1) Å, $V = 491.70$ (1) Å³, $Z = 4$, $D_x = 6.197 \text{ g cm}^{-3}$, 1907 reflections included, $R_{wp} = 0.0449$, $R_{\text{exp}} = 0.0293$. The crystal structure of Y_2BaCuO_5 has been refined from time-of-flight neutron powder diffraction data using Rietveld analysis. Our results confirm the structure determined earlier by X-ray work and permit a more precise determination of the position, occupancy, and temperature factor of atoms in this compound.

The Y_2BaCuO_5 compound was first discovered by Michel & Raveau (1982) and later became known as the 'green

phase' or '211' phase (Hazen *et al.*, 1987) in the study of the $\text{Y}_2\text{O}_3\text{-BaO-CuO}$ system where the high- T_c superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ ('123' phase) was found (Wu *et al.*, 1987). The 211 phase is a semiconductor (Cava *et al.*, 1987) and exhibits magnetic ordering at 15 K (Weidinger *et al.*, 1988). The crystal structure of this compound (space group *Pbnm*) was solved by Michel & Raveau (1982) from powder X-ray diffraction data and later confirmed by Hazen *et al.* (1987) from single-crystal X-ray diffraction data. However, these X-ray measurements may have limited sensitivity to O atoms. Indeed, the original X-ray studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ did not reveal the unique ordering of oxygen vacancies later determined by neutron powder diffraction (Jorgensen, 1987). Additionally, the single-crystal work on Y_2BaCuO_5 provided only the atom positions with no estimates of uncertainties being reported (Hazen *et al.*, 1987). The site occupancies were not refined although microprobe analysis indicated

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